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DEPARTMENT OF THE ARMY

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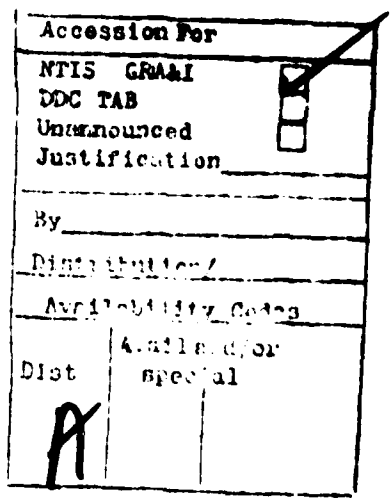
ABSTRACT

We show that it is indeed possible to use underdamped hard modes of high symmetry to determine quantitatively the temperature dependence of the order parameter in a structural phase transition (SPT). The example chosen is that of the SPT in NbO_2.



Light scattering methods have proven to be very effective in the study of phase transitions[1]. Soft mode Raman spectroscopy in particular has been extensively used because it allows a direct determination of the temperature dependence of the order parameter $\eta(T)$ which is the physical quantity of interest. This method should be quite general as any structural phase transition (SPT) can be described in terms of one or more unstable "soft" optical phonons. Experimentalists, however, have found that it had obvious limitations, namely that the "soft" mode cannot always be identified, can be overdamped or can be masked by the splitting of some other mode. Recently, Petzelt and Dvorak[2] have proposed that for non-degenerate modes

$$\Delta\omega(T) = \omega_h(T) - \omega_h(T_c) \propto \eta^2(T)$$

where $\omega_h(T)$ is the frequency of a "hard" Raman mode at various temperatures and T_c is the critical temperature. This elegant result, derived from a simple group-theoretical analysis, suggests that the much simpler hard mode Raman spectroscopy (HMS) can be used when soft mode Raman spectroscopy (SMS) is impossible.

We report here the first quantitative verification of the above relationship. We show that in at least one SPT, that exhibited by NbO_2, it holds true quite far away from T_c despite the fact that Petzelt and Dvorak[2] had limited their treatment to lowest coupling terms and consequently to T near T_c. Moreover, we confirm the interesting results of Pynn and

Axe[3] who had determined in the case of NbO_2 that the critical exponent β, away from T_c, had the value 0.19 ± 0.02 which is significantly different from the usual value of 0.5.

NbO_2 exhibits a semiconductor to metallic transition at T_c = 809°C which has been widely investigated[4]. Extensive structural studies[3,4,5] have been carried out and, because Mukamel[6] had pointed out that the SPT could be described by a four-component order parameter, Pynn and Axe[3] have carried out a special study of the critical exponent β. It showed that over a range of temperatures from near T_c down to 400°C below T_c the value of β is 0.19 ± 0.02 as stated above. However, within 7°C of T_c it is $0.4^{+0.04}_{-0.07}$ exhibiting a quite unusual crossover. The earlier work of Shapiro, et al[5] had already indicated that the "soft" mode could be overdamped. Our preliminary Raman study apparently confirmed this (Fig.1) since the only soft mode manifestation which we observed was an increase in the Rayleigh scattering which augments with temperature as one approaches T_c. This difficulty motivated us in testing the suggestion made by Petzelt and Dvorak[2].

The oriented single crystals used in these studies were grown by a method described elsewhere[7]. A special furnace was built which allowed for data collection in the back-scattering configuration while the sample was heated under a protective gettered atmosphere (10^{-3} torrs Ar/H_2 in conjunction with tantalum sample holders). The temperature stability of the furnace was of the order of ±1°C while the reported sample

temperature, which was measured by a chromel-alumel thermocouple and compared to a calibrated optical pyrometer at high temperatures, is estimated to be accurate to within only about $\pm$5°C. The 5145 Å line of an Ar^+ ion laser was used to excite the spectra with the laser power at the sample kept below 100mW in order to minimize laser heating. The scattered light was analyzed by a one-meter Jarrell-Ash double monochromator and detected by an RCA (31034-04) cooled photomultiplier. Phase sensitive detection was used to separate the signal due to the Raman scattered light from the signal due to the light emitted by the furnace.

The modes of A_{1g} symmetry were judged to be particularly desirable for this study as they have the same symmetry as the soft mode and are more likely to be strongly coupled to it[8]. The Raman spectrum of NbO_2 exhibits two strong A_{1g} modes at 168 and 347 cm^{-1} at room temperature. While similar results have been obtained for both of these modes as a function of temperature, only the results for the mode at 168 cm^{-1} will be presented here.

Part of the Raman spectrum of NbO_2, including the first A_{1g} mode, is shown in Fig. 1 for three different temperatures. The broadening of the central line, evident in Fig. 1, was shown to be reversible and, therefore, probably corresponds to the contribution of the overdamped soft phonon rather than to an extraneous cause. This broadening of the central peak made the precise determination of the frequencies of the hard

A_{1g} photon particularly difficult since it also became increasingly broadened with temperature. The complex lineshape was analyzed by obtaining a least squares fit to an equation for the intensity of the form

$$I(\omega) = S\gamma^2\omega(\bar{n}(\omega)+1) \; / \; (\omega^2+\gamma^2) \; + A/\{(\omega-\omega_h(T))^2 + \beta^2\}.$$

S and γ are the mode strength and damping constant respectively for the Debye function representing the soft mode contribution while A is the mode strength and β the damping constant for the Lorentzian representing the hard mode (A_{1g}) contribution. $\bar{n}(\omega) = \{\exp(\hbar\omega/kT) - 1)\}^{-1}$ is the usual Bose-Einstein factor evaluated at ω. The results for $\omega_h(T)$ for the A_{1g} mode at 168 cm^{-1} (room temperature) are shown in Fig. 2. They were fitted using the equation

$$\Delta\omega(T) = \omega_h(T) - \omega_h(T_c) = \alpha(T_c-T)^{\beta}$$

where $\omega_h(T_c)$, α, and β were parameters left to adjust while T_c was taken to be 809°C. The optimum values returned by the curve fitting for $\omega_h(T_c)$ and β, averaged over four different runs, are:

$$\omega_h(T_c) = 131 \pm 0.6 \; cm^{-1} \text{ and } \beta = 0.39 \pm 0.05.$$

The data in Fig. 2 replotted in the coordinates $\Delta\omega$ vs. $(T_c-T)^{0.39}$ are shown in Fig. 3.

Now over part of the range of temperature which has been explored in the present work, the results of Pynn and Axe[3] indicate that the temperature dependence of the order parameter is of the form

$$\eta(T) \propto (T_c-T)^{0.19}.$$

Thus it follows that over an extended range of temperature from near T_c down to 770°C below T_c the present results are in excellent agreement with the previous results of Pynn and Axe[3] if one assumes

$$\Delta\omega(T) \sim \eta^2(T).$$

This result is doubly important, first because it verifies the suggestion of Petzelt and Dvorak in a particularly unusual case and, second, because it seems to extend the validity of the relationship $\Delta\omega(T) \propto \eta^2(T)$ to quite far away from T_c.

In conclusion, we have established that HMS can be sucessfully used to determine the temperature dependence of the order parameter in materials where SMS is not possible. Taking into consideration the fact that NbO_2 is a particularly unfavorable case, both because the measurements had to be carried out in back scattering and the transition temperature is very high, the above result seems to open a whole new dimension in the Raman spectroscopic investigation of SPT critical phenomena.

The results reported above are, in fact, extremely general. Since they were obtained, we have been able to do further work under ONR sponsorship and it has become clear that: 1) in NbO_2 the mode we have been following is, in fact, interactive. While anharmonic coupling with the soft mode gives rise to the effect we have observed and makes the hard mode frequency vary

like the square of the order parameter, at higher temperature direct coupling prevails. This is best represented by a bi-linear coupling term. It means, in effect, that at high temperature we have the emergence of a dynamic central peak. In work done since the end of the present funding period and under a different sponsorship (ONR), we have been able to analyze this central peak. The total work is to be published soon as one or two papers with proper credits to the funding origin. 2) the phenomena which we have begun to analyze here is, in fact, of great generality and present features similar to that which occur in linear organic conductors, in ferroelectrics of the improper type, in spin glasses transformations, in valence fluctuations, in polyacetylene, in brief, in all phenomena where the driving mechanism involves the generation and propagation of an excitation in the presence of disorder.

Conclusions

At this stage of our understanding of the phase transition mechanism in NbO_2 we can clearly make a connection between the polaron mediated field switching, which we had originally used to analyze the early switching measurements, and the light scattering results. These results show that optical phonons are interacting with a lower excitation that may simply be a sea of polarons and that this interaction drives the transition.

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Figure Captions

Fig.1 Representative low frequency Stokes Raman spectrum of the $A_1 + E$ modes of NbO_2 at three different temperatures. The spectra taken at T = 515°C and T = 714°C have been displaced vertically for clarity. The feature labelled G is of instrumental origin.

Fig.2 The peak position of the A_{1g} Raman line at 168 cm^{-1} (room temperature) versus temperature.

Fig.3 $\Delta\omega(T) = \omega_h(T) - \omega_h(T_c)$ versus $(T_c-T)^{\beta}$ with T_c = 809°C, $\omega_h(T_c)$ = 131 cm^{-1} and β = 0.393 for the A_{1g} Raman line at 168 cm^{-1} (room temperature).

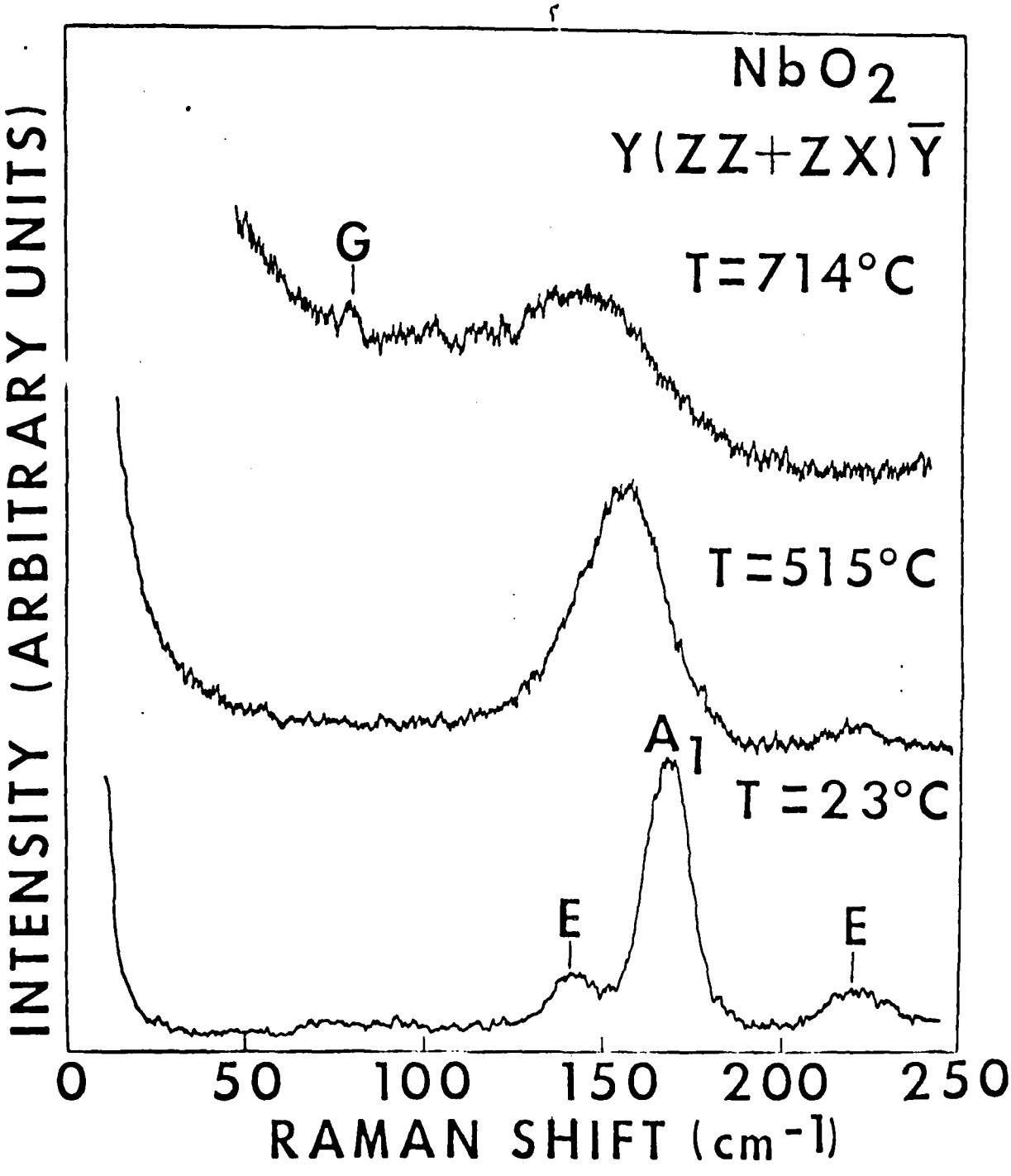
NbO2
Y(ZZ+ZX)Y
G
T=714°C
T=515°C
A1
T=23°C
E
E
INTENSITY (ARBITRARY UNITS)
0
50
100
150
200
250
RAMAN SHIFT (cm-1)

Fig. 1

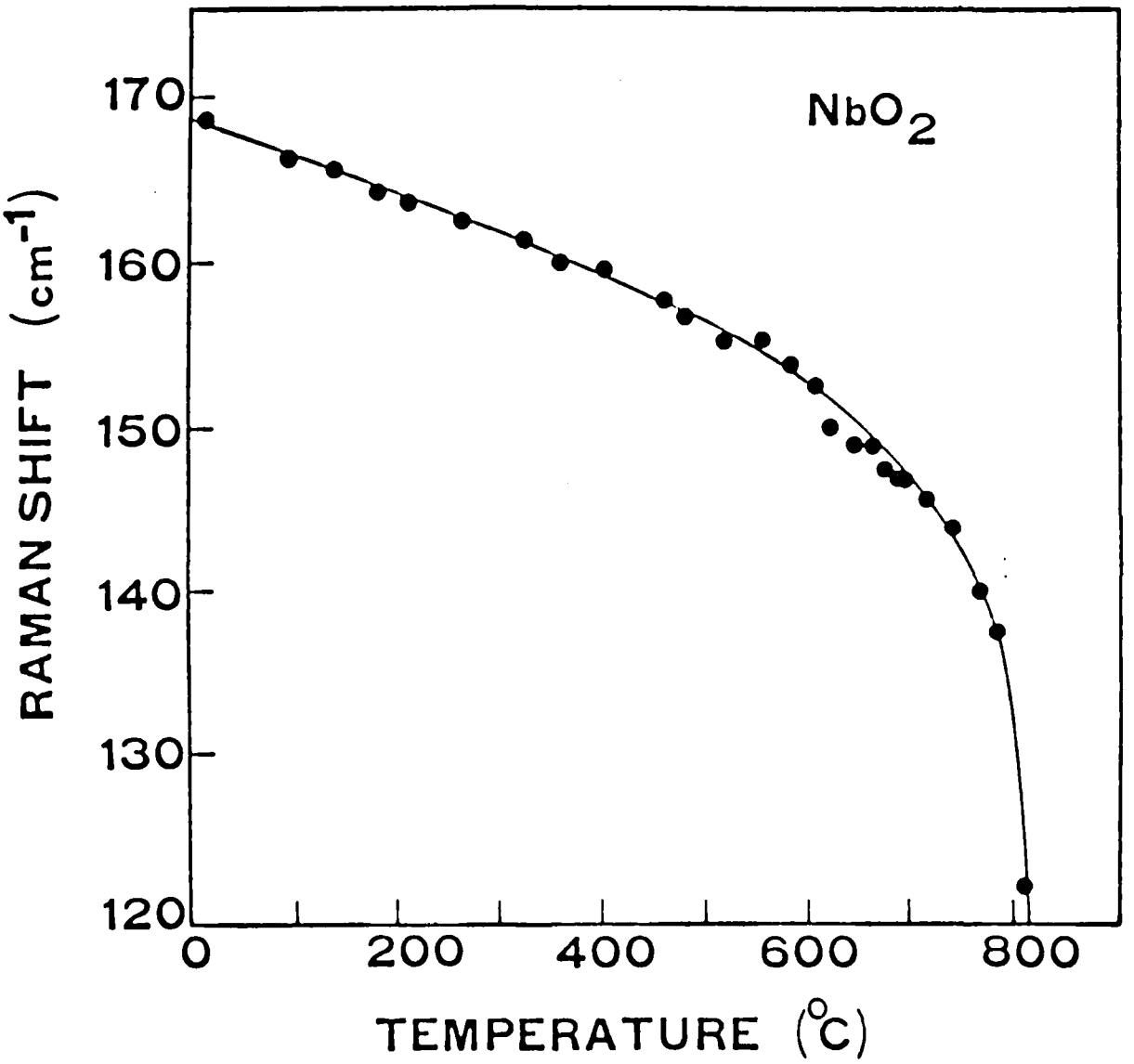
NbO2
RAMAN SHIFT (cm-1)
170
160
150
140
130
120
0
200
400
600
800
TEMPERATURE (°C)

Fig. 2

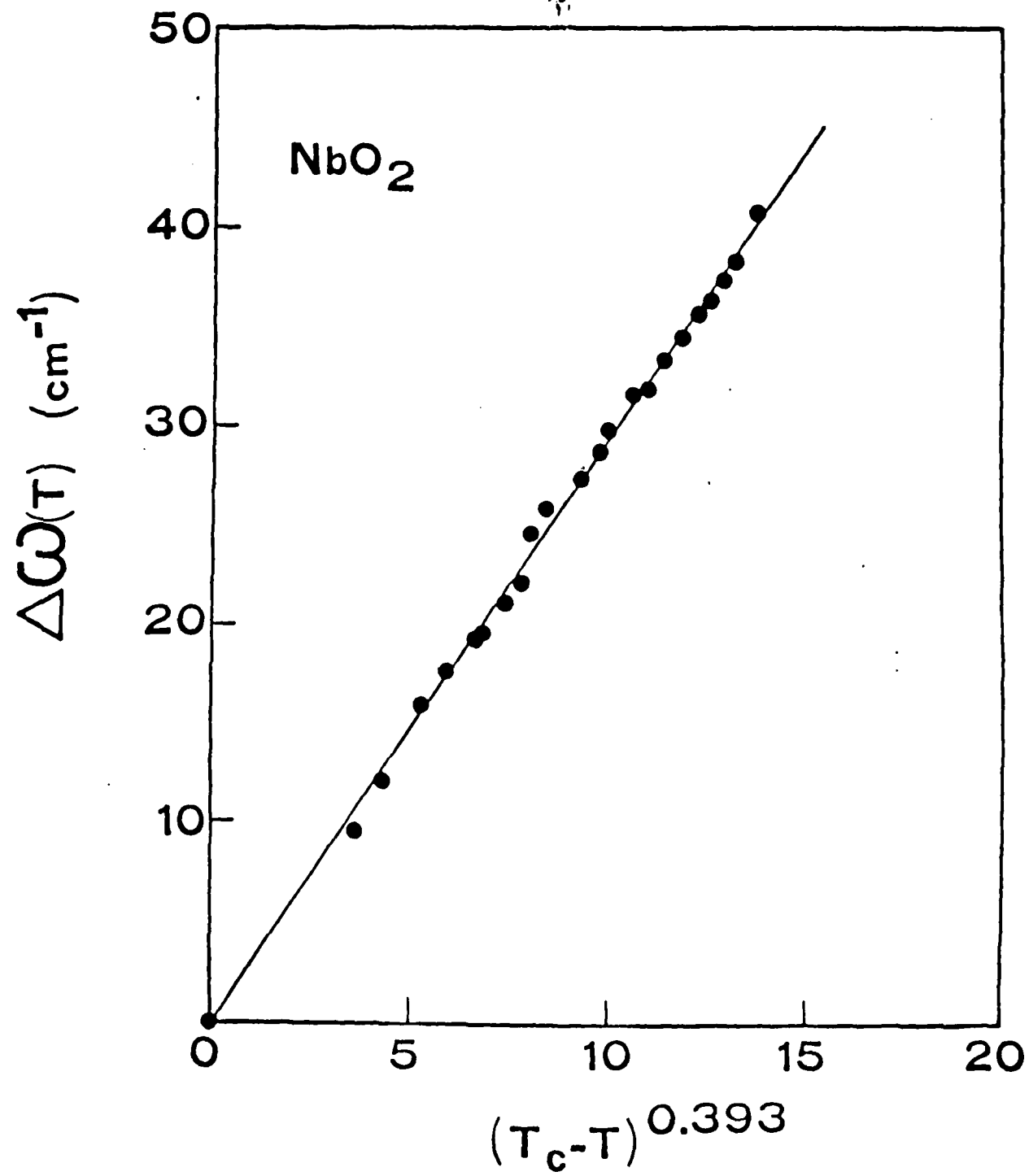

Fig. 3

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PII Redacted [redacted]

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1972-9/76	Director of the Maxwell R. Maybaum Institute for Material Sciences and Quantum Electronics
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1964-1971	Solid State Division of Massachusetts Institute of Technology Lincoln Laboratory Working in the electronics materials group with John B. Goodenough
1962-1964	Group leader at C.A.E. (European Subsidiary of T.R.W.)

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